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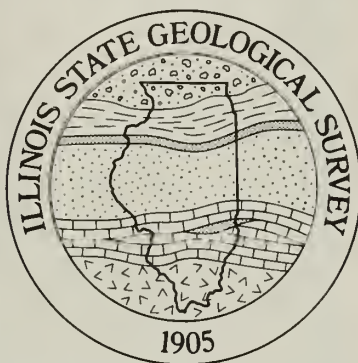
FINAL TECHNICAL REPORT  
September 1, 1989 through August 31, 1990

**CHARACTERIZATION OF THE ORGANIC SULFUR  
IN MACERALS AND CHARS**

Principal Investigator: Richard D. Harvey, ISGS  
Co-investigator: Ilham Demir, ISGS  
Project Monitor: Daniel D. Banerjee, CRSC

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## ABSTRACT

Three Illinois Basin Coal Sample Program (IBCSP) coals (IBC-101, IBC-102, IBC-107) were crushed to -20 mesh ( $<850\ \mu\text{m}$ ) and the 20 to 35 mesh (500 to  $850\ \mu\text{m}$ ) fractions were separated for characterization of the distribution of their organic sulfur contents. Heat-treatment (charring) runs were carried out on the samples at temperatures ranging from  $250^{\circ}\text{C}$  to  $550^{\circ}\text{C}$  using a rotary pyrolysis system. The concentration of organic sulfur around pyrite grains included within macerals in the untreated coals, as well as pyrite grains and pores, in their heat treated products was determined. On the average, the organic sulfur content increased near pyrite grains after the coals were charred at  $550^{\circ}\text{C}$ , indicating that some of the pyritic sulfur released during charring is combined with the organic matrix rather than being emitted to the atmosphere.

The sulfur isotope data confirm the movement of pyritic sulfur into the macerals during heat treatment of the coals. The results of the isotope analyses of organic sulfur in the IBC-107 coal, prior to and after charring, indicate that about 18 percent of the organic sulfur remaining in the  $550^{\circ}\text{C}$  chars is sulfur that was originally pyritic sulfur.

The residue from the low-temperature ashing of the fresh samples of all nine of the IBCSP coals were analyzed for their size distribution with a computer controlled particle size analyzer (Microtrac). The results document significant variations in size of minerals from one sample to another. The method of analysis has much promise for use in coal testing. It has potential use in enabling the prediction of the fineness of crushing that would be needed to liberate a designated portion of the mineral matter. But the apparent inconsistencies we observed for the mean sizes, when measured on the volumetric and on the area bases, needs to be evaluated in a future study. In addition, the reproducibility of the method, when applied to minerals in coal, needs to be determined.

## EXECUTIVE SUMMARY

The overall objective of this project is to determine the spatial distribution of organic sulfur with respect to various types of physical features in coals and their heat-treated products (chars). The specific tasks for the current year are:

1. Determine and compare the spatial distribution of organic sulfur in macerals adjacent to pyrite grains of measured size in three different Illinois Basin coals and their chars.

2. Determine and compare the significance of the particle size distribution of the mineral matter in all nine IBCSP samples.

To determine sulfur mobility during charring we had initially planned to make our analyses on selected macerals in the raw coal specimen, then char that specimen, and analyze the same macerals again. We tested four different mounting cements that are stable at desired charring temperatures: Sauereisen electrical cement, Thermocraft ceramic cement, struvite, and carbonate (hydrated lime -  $\text{CO}_2$ ). But either the polishing characteristics of the cements were unacceptable, or the calcium in the cement contaminated the macerals. A suitable way to char specimens embedded in a temperature stable cement to monitor sulfur mobility around a single grain of pyrite, at different temperatures, was not feasible. We resolved this by charring crushed particles and analyzing a many of them to obtain statistically significant mean values.

Samples of the three coals (IBC-101, IBC-102, IBC-107) were first crushed to -20 mesh ( $<850\ \mu\text{m}$ ) and then the 20 - 35 mesh (500 to  $850\ \mu\text{m}$ ) fraction of each was separated for characterization. Charring runs were carried out on the samples at temperatures ranging from  $250^\circ\text{C}$  to  $550^\circ\text{C}$  using an available rotary pyrolysis apparatus. Each sample of raw and charred coal was mounted in regular epoxy material for the microscopical and SEM-EDX study.

A total of 996 spots around 115 pyrite grains and 50 spots around 5 pores, included in macerals of raw coals and of their chars were analyzed by SEM-EDX methods. The pyrite particle size was also determined in the SEM for the samples. The SEM-EDX results indicate that the organic sulfur content increases near pyrite grains when the coals are charred at  $550^\circ\text{C}$ , suggesting that some of the pyritic sulfur released during heating is subsequently combined with organic matter. The  $\delta^{34}\text{S}$  values of the organic sulfur in the IBC-107 coal support this conclusion. The organic sulfur  $\delta^{34}\text{S}$  values in the  $550^\circ\text{C}$  chars of that sample changed significantly relative to the original values in the raw coal. The  $\delta^{34}\text{S}$  results indicate about 18 percent of the organic sulfur in the  $550^\circ\text{C}$  chars is sulfur that had been pyritic sulfur in the untreated coal.

coal

Of scientific and perhaps engineering importance, this work documents a trend of decreasing organic sulfur content within the maceral material around pyrite grains of increasing size. The pyrite considered here is restricted to the disseminated type, the ones enclosed within macerals.

Fresh samples of all nine Illinois Basin Coal Sample Program coals were crushed to top size of 850  $\mu\text{m}$  and then ashed in an oxygen plasma at  $<150^{\circ}\text{C}$ . The residue from the ashing, which consists of unaltered mineral grains from the coal, were then analyzed for their size distribution with a computer controlled particle size analyzer (Microtrac). As we expected, these unique results (reported here for the first time) indicate there is a significant variation in size of minerals in the different samples; and because this method of analysis is relatively easy and rapid to carry out, it has much promise for use in coal testing. It has potential use for engineers to predict the fineness of crushing that would be needed to liberate a designated portion of the mineral matter. But the observed inconsistencies between the mean size data (volumetric versus area bases) must be evaluated further in future studies. In addition, the reproducibility of the method, when applied to minerals in coal, needs to be determined.

## OBJECTIVES

The overall objective of this project is to determine the spatial distribution of organic sulfur with respect to various types of macerals and mineral particles, mostly pyrite, and of pores in coals and their heat-treated products (chars). The specific tasks for the current year are:

1. Determine and compare the spatial distribution of organic sulfur in macerals, especially vitrinite macerals, adjacent to pyrite mineral grains of measured size in three different Illinois Basin coals and their chars; also the organic sulfur adjacent to pores in the chars. The chars were to be prepared from the coals at temperatures between 250° and 550° C. To accomplish this objective we planned to use the SEM-EDX procedures that we developed during the previous year [Harvey et al., 1989]. The results from the SEM-EDX studies were to be supplemented with isotopic analysis of IBC-107 coal, an isotopically labeled sample of coal.

2. Determine and compare the significance of the particle size distribution of the mineral matter in all nine IBCSP samples. To accomplish this objective, we planned to separate the mineral matter from each of the nine IBCSP coals by low temperature ashing in an oxygen plasma at <150°C. The separated mineral grains could then be analyzed for their size distribution with a computer controlled particle size analyzer (Microtrac).

## INTRODUCTION AND BACKGROUND

Certain fundamental questions regarding the physical characteristics and interactions between the main building blocks of coal remain largely unanswered, especially the amount of sulfur in different macerals and adjacent to mineral impurities in untreated coals and their heat-treated products (chars).

Knowledge of the spatial distribution of organic sulfur with respect to other physical features, including the size and type of mineral impurities, in coal and chars is needed to understand the heterogeneous reactions that are involved in desulfurization and producing fuels and chemicals from coal. The results from this two-year project will provide valuable support data for those who are designing new, more effective bench scale processes to desulfurize Illinois Basin coals. The data will also provide a geological assessment and possible correlations that may lead to useful guides to deposits of specific coal types.

Raymond and Gooley [1978] reviewed the literature on organic sulfur analysis in coal and applied a method particularly suited for use with an electron microprobe. They found good agreement between their results on vitrinite and the standard ASTM (D2492) results on the bulk coal. From 1982 to 1986 the Illinois Coal Development Board supported several

projects headed by Wert [1986] on the direct measurement of organic sulfur in coal, based on transmission electron microscopy methods [Hsieh and Wert 1985; Tseng et al., 1986; and Wert et al., 1988]. They analyzed maceral fractions, separated by a density gradient centrifugation method, and observed the mean organic sulfur content to be highest in sporinite and associated liptinites, intermediate in vitrinite, lowest in the inertinite macerals. Clark et al. [1984] measured organic sulfur in coal samples from Pennsylvania and Kentucky using an SEM-EDX technique and observed a significant correlation of organic sulfur content with increasing fluidity (maximum dial divisions per minute during Gieseler plastometer runs, ASTM D2639). Cleyale et al. [1984] found that thermal decomposition of pyrite in the range 500 and 550°C enriched the organic sulfur in the surrounding maceral in a Nova Scotia coal. Their SEM-EDX measurements detected the enrichment of the sulfur up to 15  $\mu\text{m}$  into the maceral. They concluded from these and other data that the decomposition of pyrite within coal is affected by poorly known characteristics of the particular coal and that the behavior of sulfur adsorption during heating should be examined for each coal. Wert [1985] reported such data for tests done on a sample of the Springfield Coal from Illinois. He found organic sulfur values in maceral matter near 1  $\mu\text{m}$  and 5  $\mu\text{m}$  crystals of pyrite to first decrease between 350° and 425°C and then to increase in the maceral at higher temperatures. The rate of increase was about the same for both sizes of pyrite. These experiments need to be repeated for a variety of Illinois Basin coals wherein the heating rate and time of heating are well documented, and a wider grain-size range of pyrite are tested.

Results from our previous study [Harvey, et al., 1989] provide support for the current project. We modified the procedures of the previous investigators for use in our facilities to determine the organic sulfur in coal and in identified maceral particles without separating maceral fractions with chemical solutions. The SEM-EDX results, for which a mean value for many different analysis spots in each of four different samples were determined, were proved to be in good agreement with the bulk analyses obtained by the routinely used ASTM analysis, wherein the organic sulfur is determined by difference. The ASTM method requires about 1 to 2 grams of sample. The SEM-EDX procedure has one main advantage, it permits the analysis of sulfur at spots about a 0.5  $\mu\text{m}$  or less in diameter. The results for individual macerals in five Illinois Basin coals showed the organic sulfur content to be the highest in sporinite intermediate in vitrinite, and lowest in inertinite group macerals.

We are not aware of any significant data on the size distribution of mineral matter in Illinois coals, aside from data on pyrite [Harvey and DeMaris, 1987]. Some experiments to measure grain sizes in low temperature ashes were attempted by Gluskoter (unpublished) during the early 1970s, first with an ultrasonic sieving device and then a coulter counter, but neither method worked very well. A new type of size analyzer is now available (Microtrac), which has much promise for characterizing low temperature ashes of coals.

## EXPERIMENTAL PROCEDURES

## SEM-EDX Analyses of Raw Coals and Chars

We searched for a satisfactory mounting cement that would be stable at the desired charring temperatures and also would take a good polish, both requirements for the SEM-EDX method. We had initially planned to make our analyses on selected macerals in the raw coal specimen, then char that specimen and analyze the same macerals again. We tested four different cements: Sauereisen electrical cement, Thermocraft ceramic cement, struvite, and carbonate (hydrated lime -  $\text{CO}_2$ ). But either the polishing characteristics of the cements were unacceptable, or the calcium in the cement contaminated the macerals. We had to abandon this approach, in favor of the standard epoxy mounting method; but this meant we had to analyze many different particles in raw coal and in the heated chars to obtain statistically significant mean values.

Samples of the three IBCSP coals (IBC-101, IBC-102, IBC-107) were crushed to -20 mesh ( $<850\ \mu\text{m}$ ) and the 20 - 35 mesh (500 to  $850\ \mu\text{m}$ ) fraction of each sample was separated by sieving. Raw and charred particles were mounted in regular epoxy material for the SEM-EDX study. Fourteen charring runs were carried out on a rotary pyrolysis system under nitrogen that had been designed and assembled by Liu, Hackley and Coleman (Fig.1). Table 1 lists only those chars that were used for the SEM-EDX study. The procedures we used for the charring runs were those developed Liu et al. [1987].

**Table 1.** Parameters for Charring Experiments. The samples were dried at  $60\ ^\circ\text{C}$  in an oven overnight and then kept in a desiccator prior to the charring. Nitrogen gas was flowing with a rate of 2 L/min through the pyrolysis tube which was rotated with 20 rpm during the experiments.

| Sample No. | Split No. | Heating Temperature ( $^\circ\text{C}$ ) | Heating Period (hrs.) | Volatile Loss** (wt.%) |
|------------|-----------|------------------------------------------|-----------------------|------------------------|
| IBC-101    | 1         | 350                                      | 1                     | 8.6                    |
|            | 2         | 450                                      | 1                     | 30.8                   |
|            | 3         | 550                                      | 1                     | 36.5                   |
|            | 4         | 550                                      | 15                    | 43.7                   |
| IBC-102    | 1         | 550                                      | 5                     | 37.8                   |
| IBC-107    | 1         | 250                                      | 1                     | 3.1                    |
|            | 2         | 550                                      | 1                     | 34.0                   |
|            | 4         | 550                                      | 5                     | 36.0                   |

\* Excludes the time of raising the temperature to a given value with a heating rate of about  $40\ ^\circ\text{C}/\text{minute}$ .

\*\* %Volatile Loss was computed by subtracting the dry weight after charring from that before charring and multiplying the result by 100.

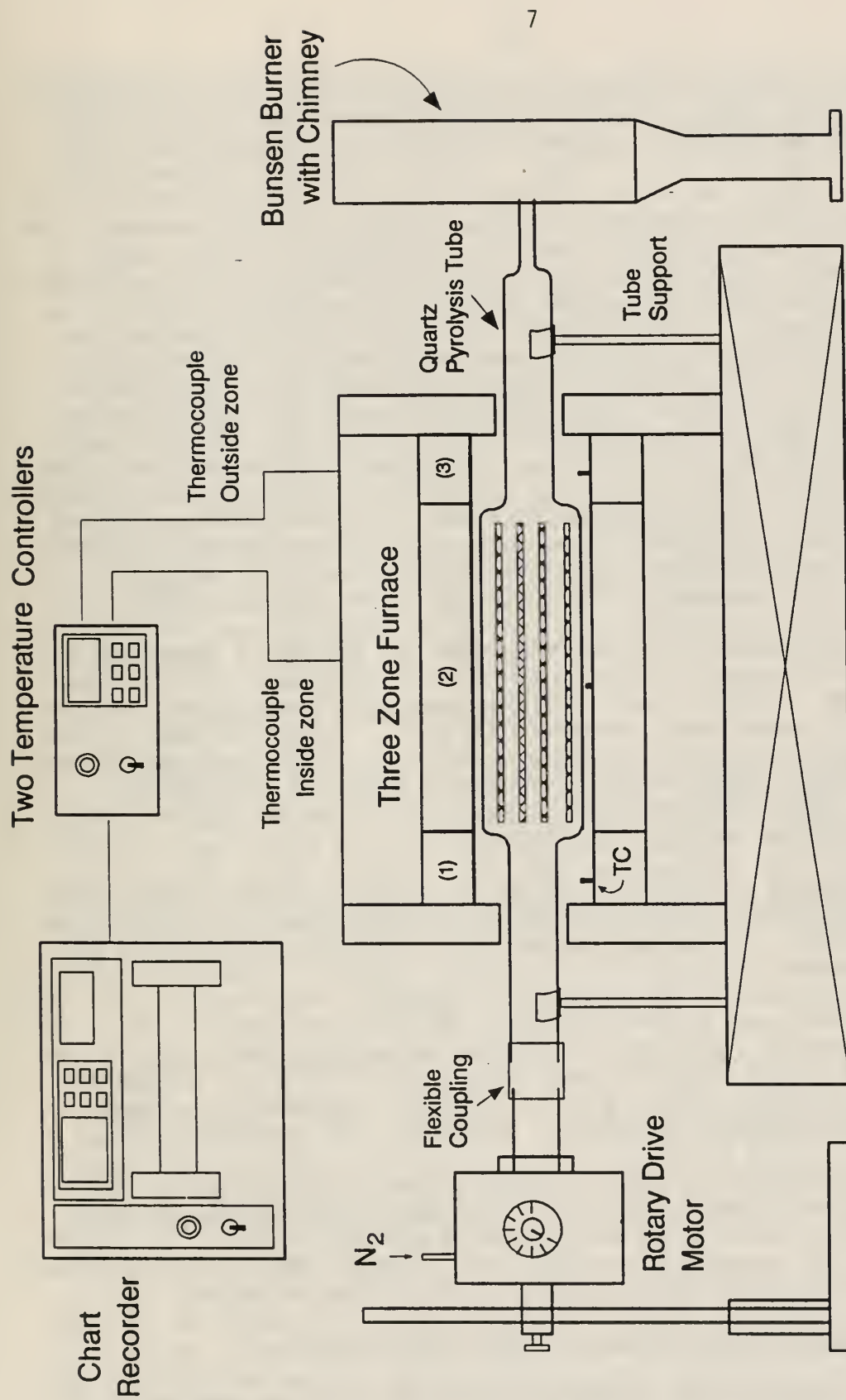


Fig. 1. Pyrolysis apparatus

The organic sulfur distribution in untreated coals and in chars adjacent to pyrite grains (pyrite or marcasite, undifferentiated) and pores was determined using SEM-EDX procedures that had been developed during the previous year [Harvey et al., 1989]. Briefly, each specimen was first examined by optical microscopy to identify spots in macerals near pyrite grains where the distribution of organic sulfur was to be measured. The specimens were then slightly etched in a low temperature asher and carbon coated in a sputter coater for enhanced image quality in the SEM. The specimen was positioned in the SEM for sulfur analysis of the identified macerals. The sulfur in mineral free spots of the maceral was determined with the aid of the computer controlled EDX analyzer. The intensity of the sulfur peak (area basis) under the EDX spectra at chosen spots was recorded. This intensity was divided by the intensity of the sulfur peak of a standard crystal of pyrite that was positioned in the SEM adjacent to the specimen. Measurement of the pyrite crystal was done every 10 minutes or less. The ratio of sulfur at the measured spots to that of pyrite was then converted to the equivalent amount of organic sulfur by plotting the ratio on a calibration curve. The curve had been previously made by plotting the same ratio for standard specimens of known organic sulfur contents [Harvey et al., 1989].

The three untreated coals were analyzed by the SEM-EDX to determine the distribution of organic sulfur adjacent to disseminated pyrite grains. Splits of the untreated coals were then exposed to temperatures between 250° to 550° C under inert atmosphere (N<sub>2</sub> gas). The heated samples were cooled, mounted in epoxy, and again spots in the organic matter adjacent to mineral grains were analyzed for organic sulfur by the SEM-EDX procedure. Spots adjacent to pores that were formed during the heating were also analyzed in selected specimens.

The occurrence of pyrite grains below the maceral surface, hidden from microscopical view, were often detected by the presence of iron (Fe) in the EDX spectra. To evaluate the organic sulfur at all such spots we measured the area ratio of Fe to S peaks of the nearest visible pyrite and subtracted an amount of sulfur from the spot, equivalent to detected iron in proportional to the iron/sulfur of the nearby pyrite. While we report the results below on a dry mineral matter free basis, some of the data are not necessarily on a completely pyrite-free basis. Furthermore, traces of elemental sulfur, which is not distinguishable from organic sulfur (carbon-bonded) are probably included in the reported value.

The size of pyrite grains that occurred adjacent to the analyzed maceral and char materials was recorded by direct measurement of the apparent diameter of the grain as it was exposed on polished surfaces in the SEM. Of course, this recorded size tends to be somewhat smaller than the true diameter of the whole grain, because of the sectioning effect.

### Sulfur Isotope Analysis of Raw and Heat-treated Samples

A split of sample IBC-107 (500-850  $\mu\text{m}$  particle size) was exposed to the same heat treatment as described above. Quantitative analysis of the two isotopic species of sulfur, <sup>32</sup>S and <sup>34</sup>S retained in the chars were

determined. Previous work of Liu, et al., [1987] determined that for this unique sample the  $^{34}\text{S}$  is characteristically abundant in the pyritic fraction and distinctly less abundant in the organic fraction of the sulfur. Thus, tests of this sample afforded a unique test of our SEM-EDX results.

Analyses of  $\delta^{34}\text{S}$  in the organic and pyritic sulfur types in IBC-107 and its heat-treated products were carried out according to the procedures outlined by Liu et al. [1987]. The coal and chars were further pulverized to <230 mesh. The sulfate sulfur was removed from the samples using a 4.8N HCl wash. The sulfate remains in the dilute acid solution and was precipitated as  $\text{BaSO}_4$ . The acid leached residues were treated with lithium aluminum hydride to remove pyritic sulfur. The pyritic sulfur is released as  $\text{H}_2\text{S}$  during this reaction, trapped in cadmium acetate solution and precipitated as  $\text{Ag}_2\text{S}$ . The organic sulfur was obtained by combusting the coal residue under pure oxygen at  $1350^\circ\text{C}$ . The organic sulfur, released as  $\text{SO}_2$ , was trapped in a 3%  $\text{H}_2\text{O}_2$  solution and precipitated as  $\text{BaSO}_4$ . For isotopic measurement the  $\text{BaSO}_4$  and  $\text{Ag}_2\text{S}$  samples were converted to  $\text{SO}_2$  by reacting with  $\text{NaPO}_3$  and  $\text{CuO}$ , respectively, at  $950^\circ\text{C}$ . The  $\text{SO}_2$  samples were analyzed on a Nuclide 6-60 ratio mass spectrometer for their isotopic composition. The isotopic results are reported relative to the Canyon Diablo Troilite (CDT) international standard. The reproducibility for the  $\delta^{34}\text{S}$  is  $\pm 0.2$  ‰.

### Size Distribution of Minerals in Coal

Fresh samples of the nine IBCSP coals were crushed to top size of  $850\ \mu\text{m}$  and then ashed in an oxygen plasma at  $<150^\circ\text{C}$ . Crushing to this size does not reduce the size of the mineral grains to any significant degree. The residue from the ashing, which consists of unaltered mineral grains from the coal, were then analyzed for their size distribution with a computer controlled particle size analyzer, Microtrac. This method is based on the measured scattering of a laser beam as it passes through a sample stirred with water.

## RESULTS AND DISCUSSION

### Distribution of Organic Sulfur Adjacent to Pyrite Grains

As expected, the volatile loss increased with increased temperature or time of exposure to heat (Table 1). Eight char and three untreated coal samples were studied under the SEM-EDX. A total of 996 spots around 115 pyrite grains and 50 spots around 5 pores were analyzed. The summary of the data are presented in Table 2 and plotted in Figs. 2 to 4.

The level of organic sulfur in the vicinity of pyrites tend to increase for IBC-101 (Fig. 2) and for IBC-102 (Fig.3), but it tends to decrease near pyrite grains for IBC-107 (Fig. 4). It may be that these are not real trends, that we have not measured the macerals around enough grains, that we may only be seeing the natural variation of sulfur. We do not believe the increased amount of sulfur very close to pyrite in

the first two sample is due to elemental sulfur as a result of oxidation of the pyrite, because the trends would have been reversed. Contrary to our data, an increased level of sulfur next to pyrite was expected in the most oxidized sample, IBC-107. This sample most oxidized of the three, because it has the lowest free swelling index (2.0 vs 4.0 for the first two samples). Further study of this aspect is needed to account for these observations.

Fig. 2 shows a general loss of organic sulfur in the 350°C char, as compared to the raw coal, as indicated by the low values relative to untreated coal for all distances from pyrite grains. At this temperature there is no observable trend of organic sulfur variation as a function of distance from pyrite. However, at 550° C, where pyrite starts decomposing, organic sulfur content increases near pyrite grains, especially with increased exposure time to heat. Similar trends are observed in Figs. 3 and 4. These results suggest that sulfur from pyrite grains migrates into adjacent macerals upon charring at 550°C.

**Table 2.** Organic sulfur as a function of distance from pyrite grains enclosed in macerals of three coals and their chars. Most numbers are means of 10 readings adjacent to 10 different pyrite grains; some are means of 7 to 9 readings.

| Coal/<br>Distance<br>( $\mu$ m) | %OS(dmmf) |            |            |      |            |     |            |     |             |     |
|---------------------------------|-----------|------------|------------|------|------------|-----|------------|-----|-------------|-----|
|                                 | raw coal  |            | 350°C, 1hr |      | 450°C, 1hr |     | 550°C, 1hr |     | 550°C, 15hr |     |
|                                 | char      |            | char       |      | char       |     | char       |     | char        |     |
|                                 | mean      | SD         | mean       | SD   | mean       | SD  | mean       | SD  | mean        | SD  |
| IBC-101/                        |           |            |            |      |            |     |            |     |             |     |
| 1                               | 3.48      | 1.3        | 2.67       | 1.0  | 3.74       | 1.5 | 3.08       | 1.1 | 4.90        | 3.4 |
| 3                               | 3.28      | 0.6        | 2.58       | 0.6  | 3.49       | 1.2 | 2.63       | 0.7 | 3.21        | 1.6 |
| 5                               | 3.38      | 0.5        | 2.66       | 0.7  | 3.21       | 1.0 | 2.48       | 0.4 | 2.86        | 1.2 |
| 8                               | 3.31      | 0.5        | 2.82       | 0.5  | 3.32       | 1.0 | 2.44       | 0.4 | 2.65        | 1.0 |
| 11                              | 3.14      | 0.6        | 2.93       | 0.6  | 3.40       | 1.0 | 2.41       | 0.4 | 2.32        | 0.7 |
| 14                              | 2.99      | 0.4        | 2.85       | 0.7  | 3.37       | 1.0 | 2.49       | 0.4 | 2.13        | 0.7 |
| 17                              | 3.12      | 0.4        | 2.68       | 0.8  | 3.27       | 1.2 | 2.40       | 0.4 | 2.09        | 0.5 |
| 20                              | 3.18      | 0.4        | 2.65       | 0.8  | 3.46       | 0.9 | 2.31       | 0.3 | 2.05        | 0.6 |
| IBC-102/                        |           |            |            |      |            |     |            |     |             |     |
|                                 |           | 550°C, 5hr |            |      |            |     |            |     |             |     |
|                                 |           | raw coal   |            | char |            |     |            |     |             |     |
|                                 |           | mean       | SD         | mean | SD         |     |            |     |             |     |
| 1                               |           | 1.83       | 0.6        | 1.63 | 1.1        |     |            |     |             |     |
| 3                               |           | 1.40       | 0.4        | 1.08 | 0.6        |     |            |     |             |     |
| 5                               |           | 1.50       | 0.4        | 0.98 | 0.4        |     |            |     |             |     |
| 8                               |           | 1.53       | 0.5        | 0.80 | 0.4        |     |            |     |             |     |
| 11                              |           | 1.48       | 0.4        | 0.77 | 0.3        |     |            |     |             |     |
| 14                              |           | 1.54       | 0.5        | 0.68 | 0.3        |     |            |     |             |     |
| 17                              |           | 1.41       | 0.3        | 0.69 | 0.3        |     |            |     |             |     |
| 20                              |           | 1.45       | 0.3        | 0.65 | 0.3        |     |            |     |             |     |

\* see footnote at the end of the table, next page.

Table 2. (cont.)

| Coal/<br>Distance<br>( $\mu\text{m}$ ) | %OS(dmmf) |     |             |     |             |     |             |     |
|----------------------------------------|-----------|-----|-------------|-----|-------------|-----|-------------|-----|
|                                        |           |     | 250 °C, 1hr |     | 550 °C, 1hr |     | 550 °C, 5hr |     |
|                                        | raw coal  |     | char*       |     | char        |     | char        |     |
|                                        | mean      | SD  | mean        | SD  | mean        | SD  | mean        | SD  |
| IBC-107/                               |           |     |             |     |             |     |             |     |
| 1                                      | 3.59      | 1.1 | 4.45        | 1.2 | 3.68        | 1.0 | 3.93        | 1.8 |
| 3                                      | 3.85      | 0.8 | 4.85        | 1.5 | 3.32        | 0.8 | 3.15        | 1.1 |
| 5                                      | 4.12      | 0.6 | 4.94        | 1.6 | 3.25        | 0.7 | 2.97        | 1.0 |
| 7                                      | 4.19      | 0.6 | -           | -   | -           | -   | -           | -   |
| 8                                      | -         | -   | 4.64        | 1.2 | 3.30        | 0.7 | 2.84        | 1.0 |
| 10                                     | 3.98      | 0.7 | -           | -   | -           | -   | -           | -   |
| 11                                     | -         | -   | 4.42        | 1.2 | 3.32        | 0.7 | 2.82        | 0.7 |
| 12                                     | 4.17      | 0.7 | -           | -   | -           | -   | -           | -   |
| 14                                     | -         | -   | 4.46        | 1.2 | 3.34        | 0.7 | 2.69        | 0.6 |
| 15                                     | 4.37      | 0.8 | -           | -   | -           | -   | -           | -   |
| 17                                     | -         | -   | 4.74        | 1.4 | 3.19        | 0.6 | 2.71        | 0.6 |
| 18                                     | 4.43      | 1.2 | -           | -   | -           | -   | -           | -   |
| 20                                     | 4.34      | 0.9 | 4.95        | 1.4 | 3.29        | 0.7 | 3.01        | 0.5 |

\* These results are unreliable because the beam current of the SEM-EDX was too unstable.

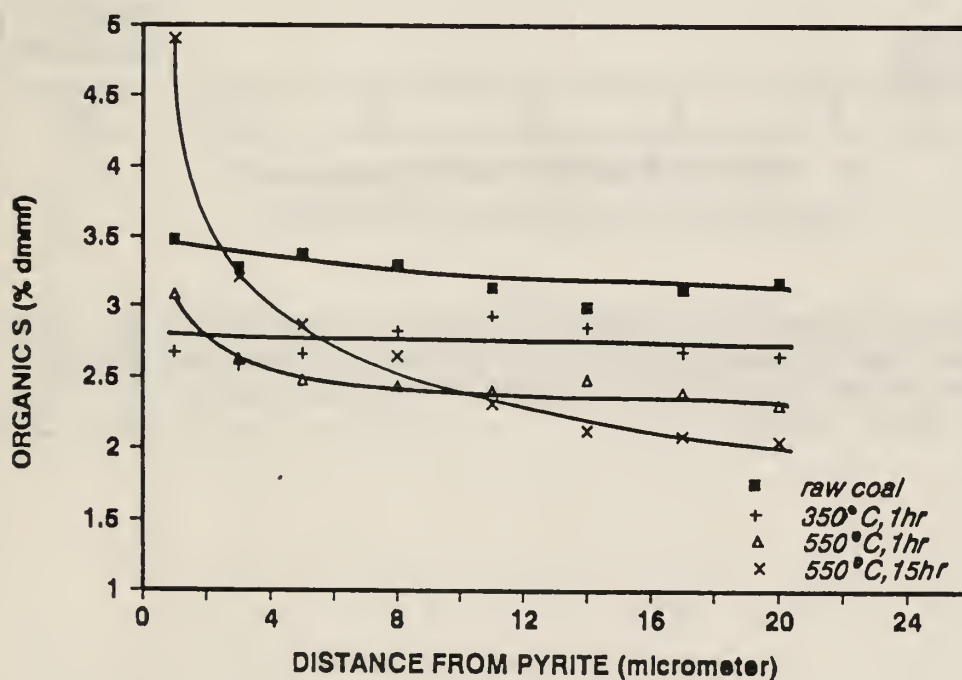


Fig.2. The distribution of organic sulfur as a function of distance from pyrite grains enclosed in the macerals of IBC-101 coal and its chars. Each datum point is the mean of 8 to 10 readings adjacent to 8 to 10 different pyrite grains.

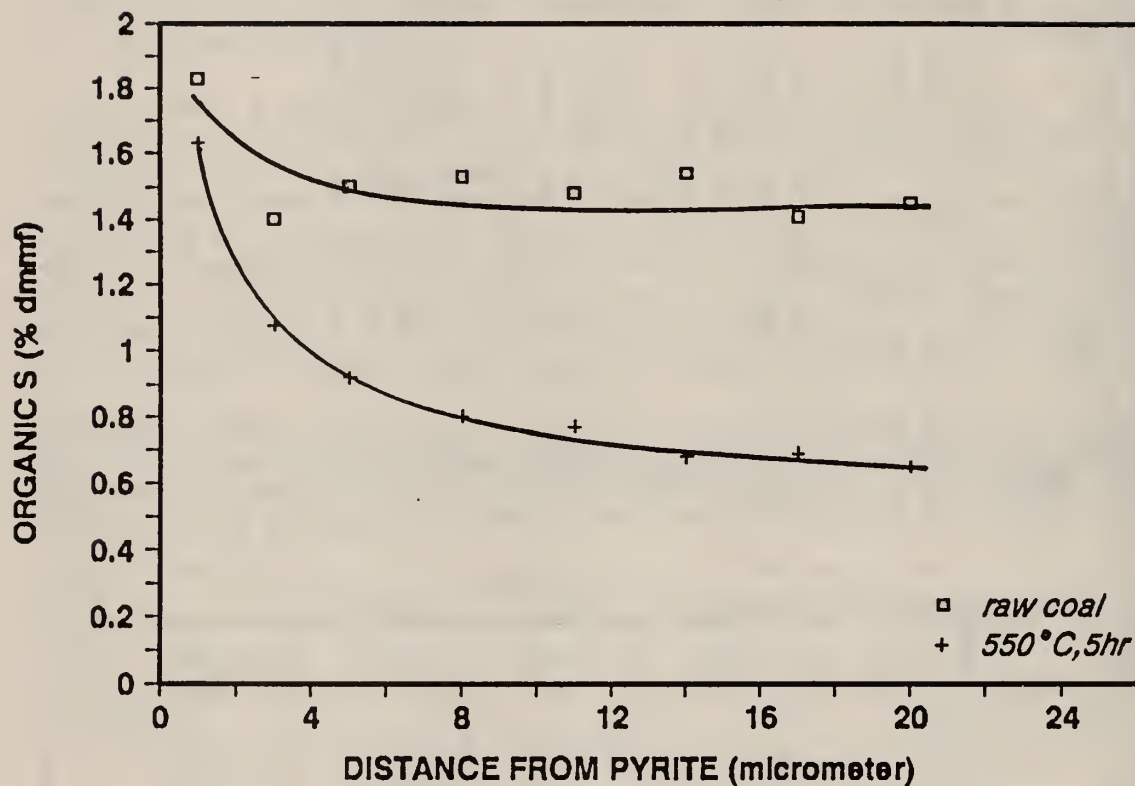


Fig.3. The distribution of organic sulfur as a function of distance from pyrite grains enclosed in the macerals of IBC-102 coal and its char. Each datum point is the mean of 10 readings adjacent to 10 different pyrite grains.

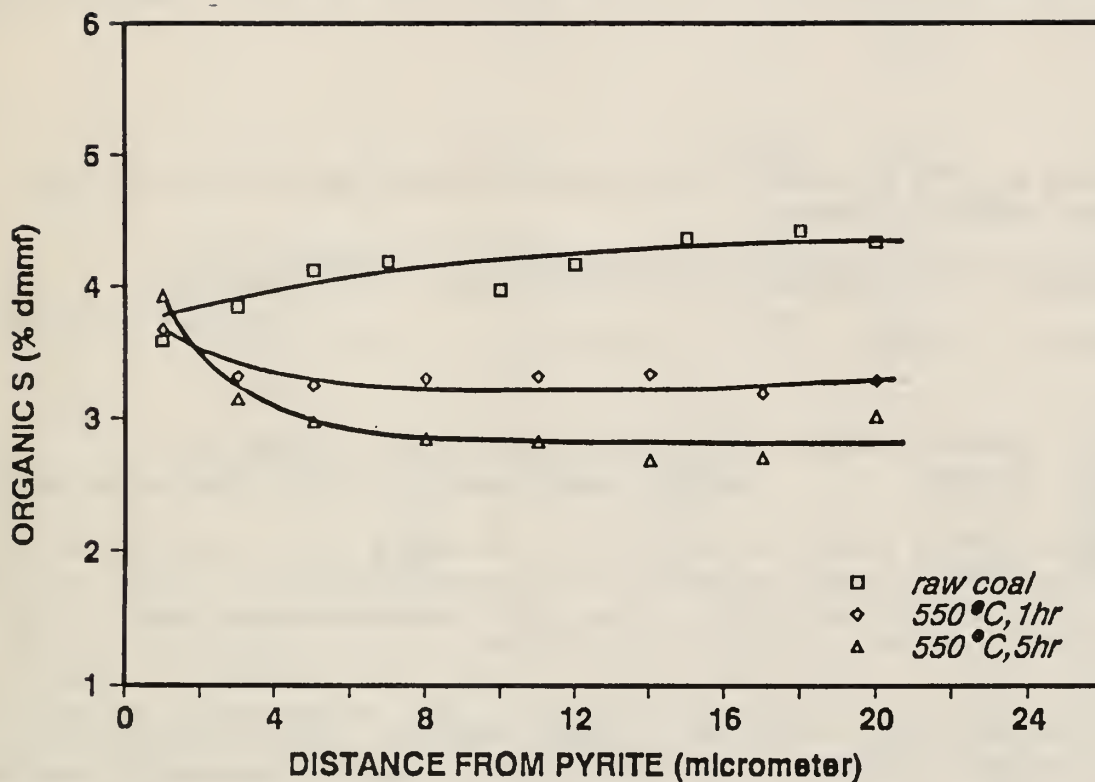


Fig.4. The distribution of organic sulfur as a function of distance from pyrite grains enclosed in the macerals of IBC-107 coal and its chars. Each datum point is the mean of 7 to 10 readings adjacent to 7 to 10 different pyrite grains.

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## Sulfur Isotope Analyses

The  $\delta^{34}\text{S}$  values of sulfur in the IBC-107 coal prior to and after heat-treatment are given in Table 3. The organic  $\delta^{34}\text{S}$  values of the 550°C chars have changed significantly relative to the original organic sulfur values.

**Table 3.**  $\delta^{34}\text{S}$  of organic sulfur extracted from IBC-107 coal and its heat-treated products.

| Sample                 | $\delta^{34}\text{S}$ Sulfate S. | $\delta^{34}\text{S}$ Pyritic S. | $\delta^{34}\text{S}$ Organic S. |
|------------------------|----------------------------------|----------------------------------|----------------------------------|
| Raw coal               | 14 ‰                             | 25.9 ‰                           | 2.2 ‰                            |
| <hr/>                  |                                  |                                  |                                  |
| Heat-treated products, | $\delta^{34}\text{S}$ (‰)        | % Pyritic S. in Org. S.          |                                  |
| 250°, 30 min           | 2.2                              | 0                                |                                  |
| 250°, 1 hr             | 2.2                              | 0                                |                                  |
| 550°, 1 hr             | 6.4                              | $\approx 18 \pm 1\%$             |                                  |
| 550°, 5 hr             | 6.4                              | $\approx 18 \pm 1\%$             |                                  |

A previous study by Liu, et al.[1987] indicates that organic sulfur is not isotopically fractionated during heat treatment, and so the observed differences (Table 3) are not due to that reaction; rather, the heavy sulfur isotope, released from pyrite grains, was absorbed by the organic matter. These results further show that the organic sulfur remaining in the 550°C chars is made up of about 18 percent sulfur which was originally pyritic sulfur. The isotope data then provides an independent confirmation for the SEM-EDX results; that is, some of the pyritic sulfur released from pyrite grains during charring at 550°C moved into the adjacent organic matrix.

## Distribution of Organic Sulfur adjacent to Pores

Limited results from two different chars indicate slightly lower mean organic sulfur concentrations near pores than away from pores (Table 4). However, whether this trend is real or artifact cannot be confirmed with the present data. For example it is possible that some of the electrons from the SEM beam hit the pore space and thus caused relatively low organic sulfur intensities near the pores. The SEM-EDX method is probably not well suited to analyze material very close to pores.

**Table 4.** Organic sulfur adjacent to pores. Each value is the mean of five readings from five different spots.

| Sample no. | Char       | Pore # | Spot distance ( $\mu\text{m}$ ) from pore | %OS  |      |
|------------|------------|--------|-------------------------------------------|------|------|
|            |            |        |                                           | mean | SD   |
| IBC-101    | 550°C, 1hr | 1      | 1                                         | 3.93 | 0.26 |
|            |            |        | 10                                        | 3.99 | 0.49 |
|            |            | 2      | 1                                         | 1.71 | 0.11 |
|            |            |        | 10                                        | 1.75 | 0.08 |
|            |            | 3      | 1                                         | 2.21 | 0.13 |
|            |            |        | 10                                        | 2.26 | 0.11 |
|            |            | 4      | 1                                         | 1.84 | 0.12 |
|            |            |        | 10                                        | 1.91 | 0.16 |
| IBC-107    | 550°C, 1hr | 1      | 1                                         | 1.63 | 0.32 |
|            |            |        | 10                                        | 1.72 | 0.16 |

### Relation between Pyrite Size and Organic Sulfur

On the average, at a distance of 12 to 20  $\mu\text{m}$  from pyrite grains, organic sulfur content tends to decrease with increasing size of pyrite grains for the three untreated coals (Figs. 5-7). This trend suggests that sulfur, in the pore waters of coal forming materials (peat or lignite stages), is preferentially drawn to a nearby seed grain of pyrite than to nearby organic matter. We interpret these results to indicate that sulfur tends to combine more efficiently with iron to make pyrite than with organic matter during coal formation. This, however, does not

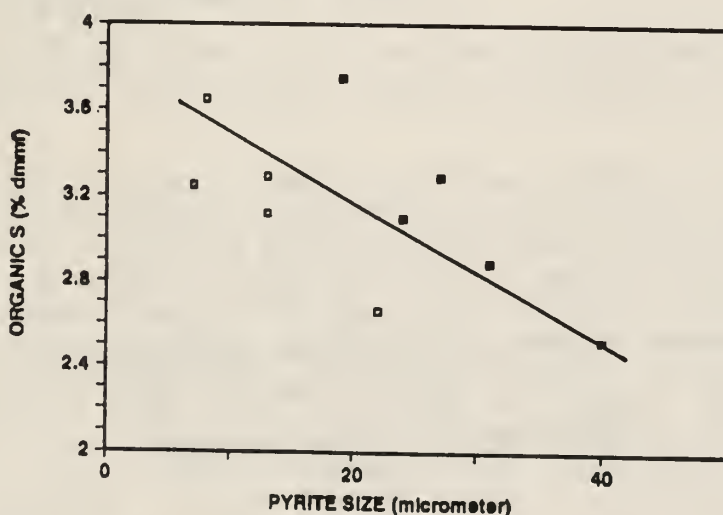


**Fig. 5.** Variation of organic sulfur in vitrinite with pyrite size in IBC-101 coal

macerals with pyrite inclusions would be poor in organic sulfur compared to the other macerals in a given coal sample. Both pyrite and organic sulfur form in high quantities in or around those pre-macerals material invaded by sulfur-rich solutions. Therefore, macerals with pyrite inclusions may, on the average, be still high in organic sulfur relative to those without pyrite inclusions for some coals.

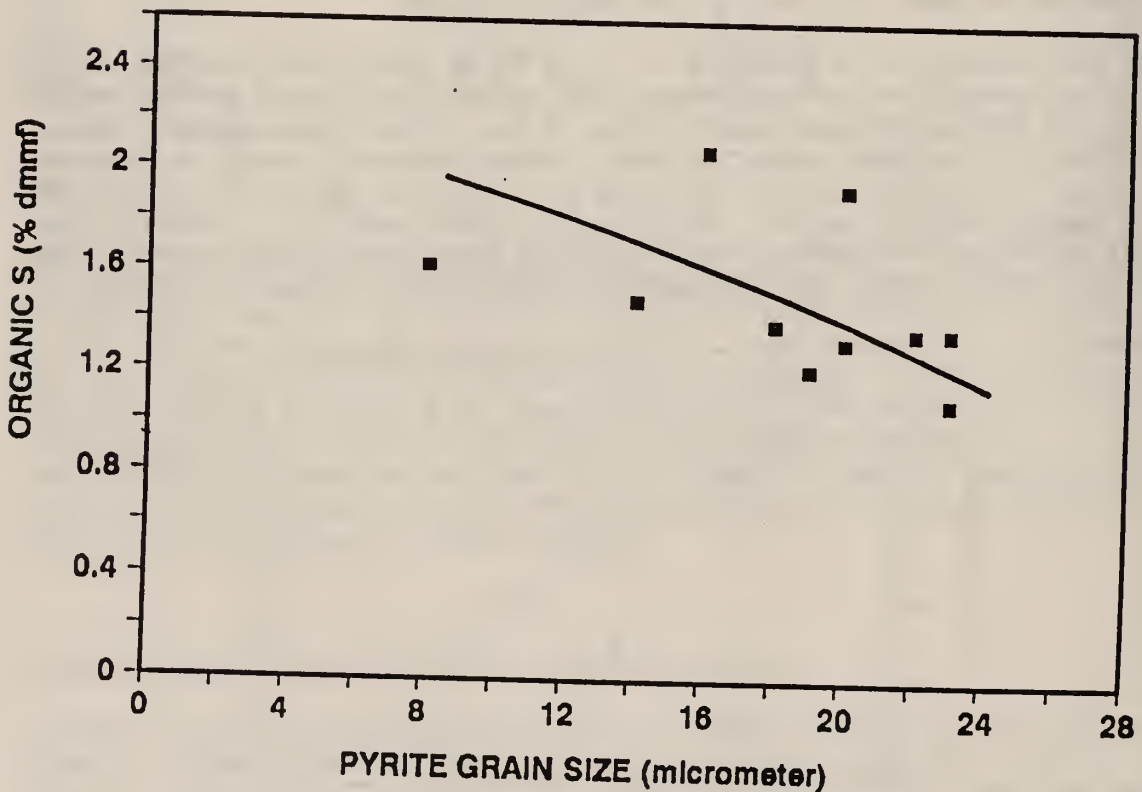


Fig. 6. Variation of organic sulfur in vitrinite with pyrite size in IBC-102 coal

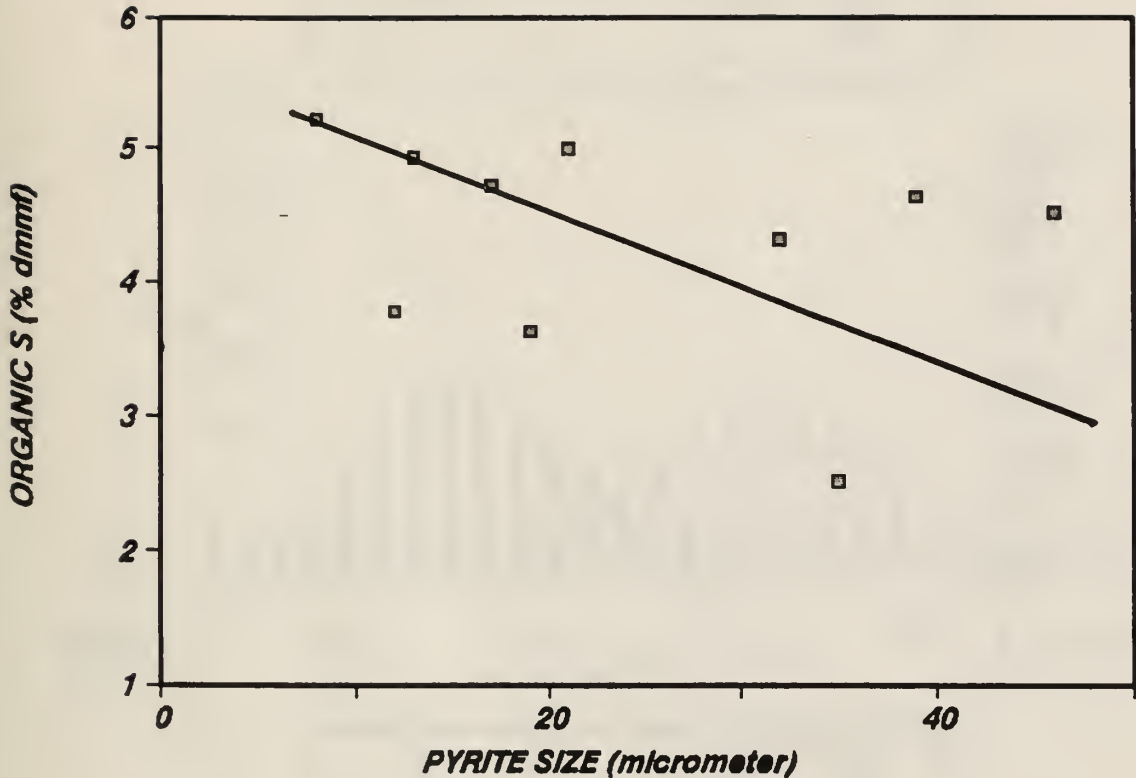


Fig. 7. Variation of organic sulfur in vitrinite with pyrite size in IBC-107 coal

### Size Distribution of Minerals in Coal

The results of the particle size analyses of the mineral matter from all nine IBCSP coals are plotted in Figs. 8-12 and they are summarized in Table 5.

These particle size data show a significant variation exists between the nine samples, but the two measures of the mean-sizes, volumetric and area measures, are not in each case consistent with each other. Sample IBC-101 has a volumetric mean-size that is twice that of IBC-102, yet their area mean-sizes are the same. The volumetric values are perhaps the best ones to consider, because these measures are more directly comparable to grain weight. In general, however, these size data are consistent with other known facts about the samples. Namely, sample IBC-104 is a run-of-mine coal with a large number of shale particles (38% ash yield), and the size data of this sample shows it to be quite large as expected. In addition, the ultra-fine grinding and cleaning that IBC-108 was exposed to resulted in the removable of all but the finest of mineral grains, which is evident by the fineness of this sample.

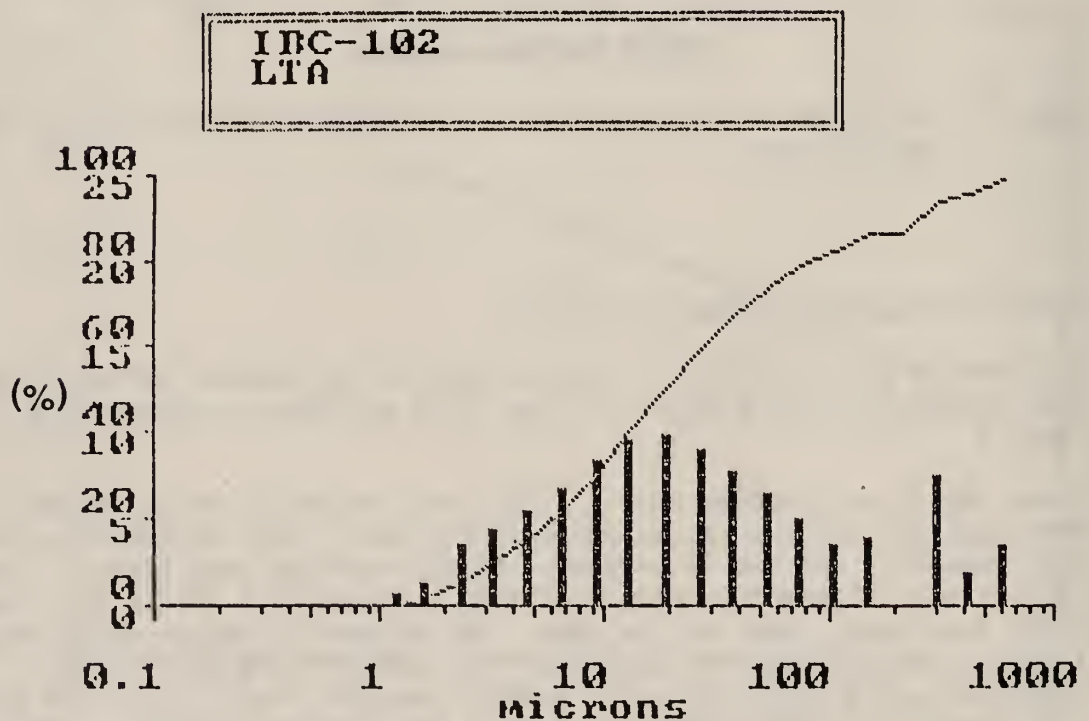
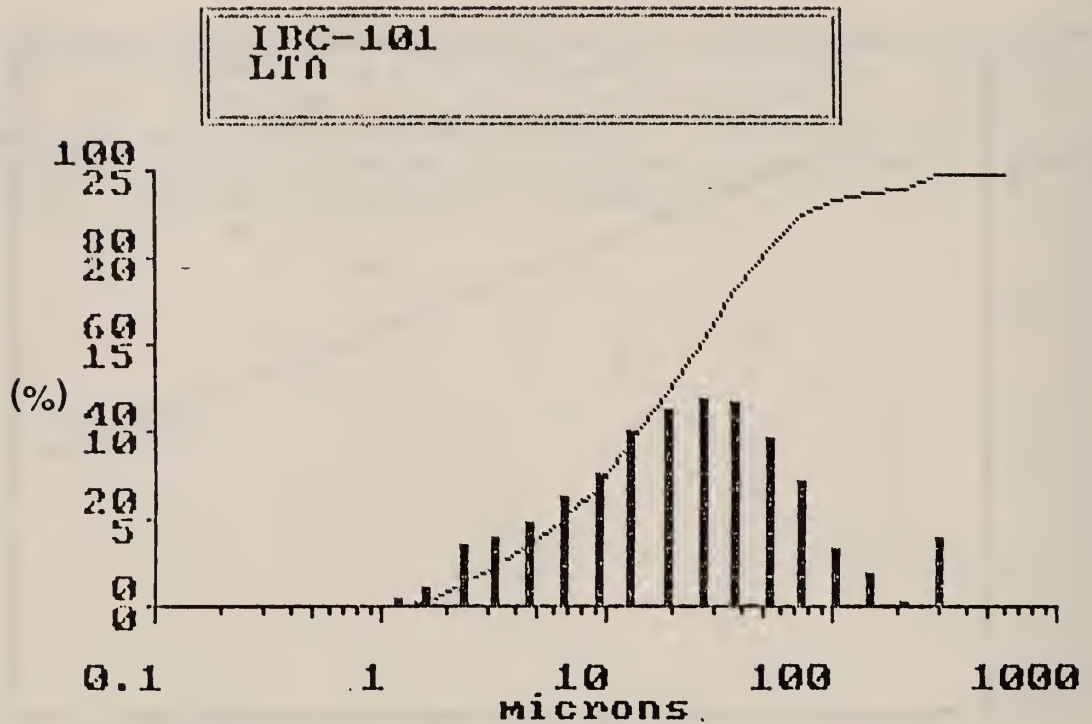


Fig. 8 . The frequency histogram of particle size classes and the cumulative size distribution of mineral matter in IBC-101 and IBC-102 coals.

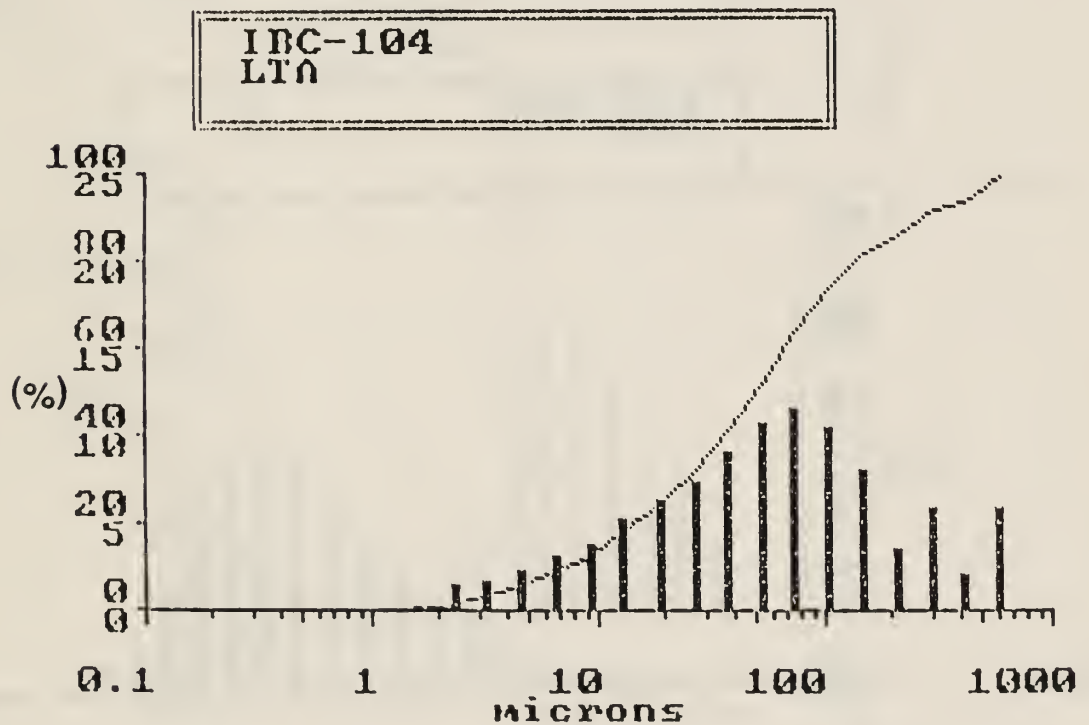
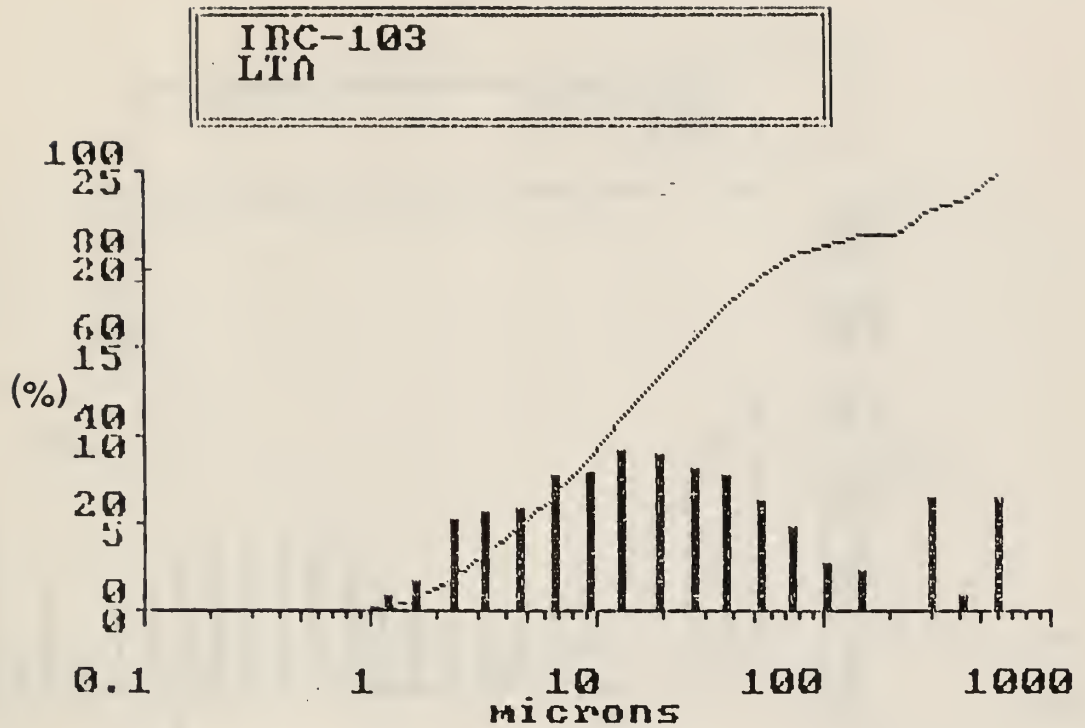


Fig. 9. The frequency histogram of particle size classes and the cumulative size distribution of mineral matter in IBC-103 and IBC-104 coals.

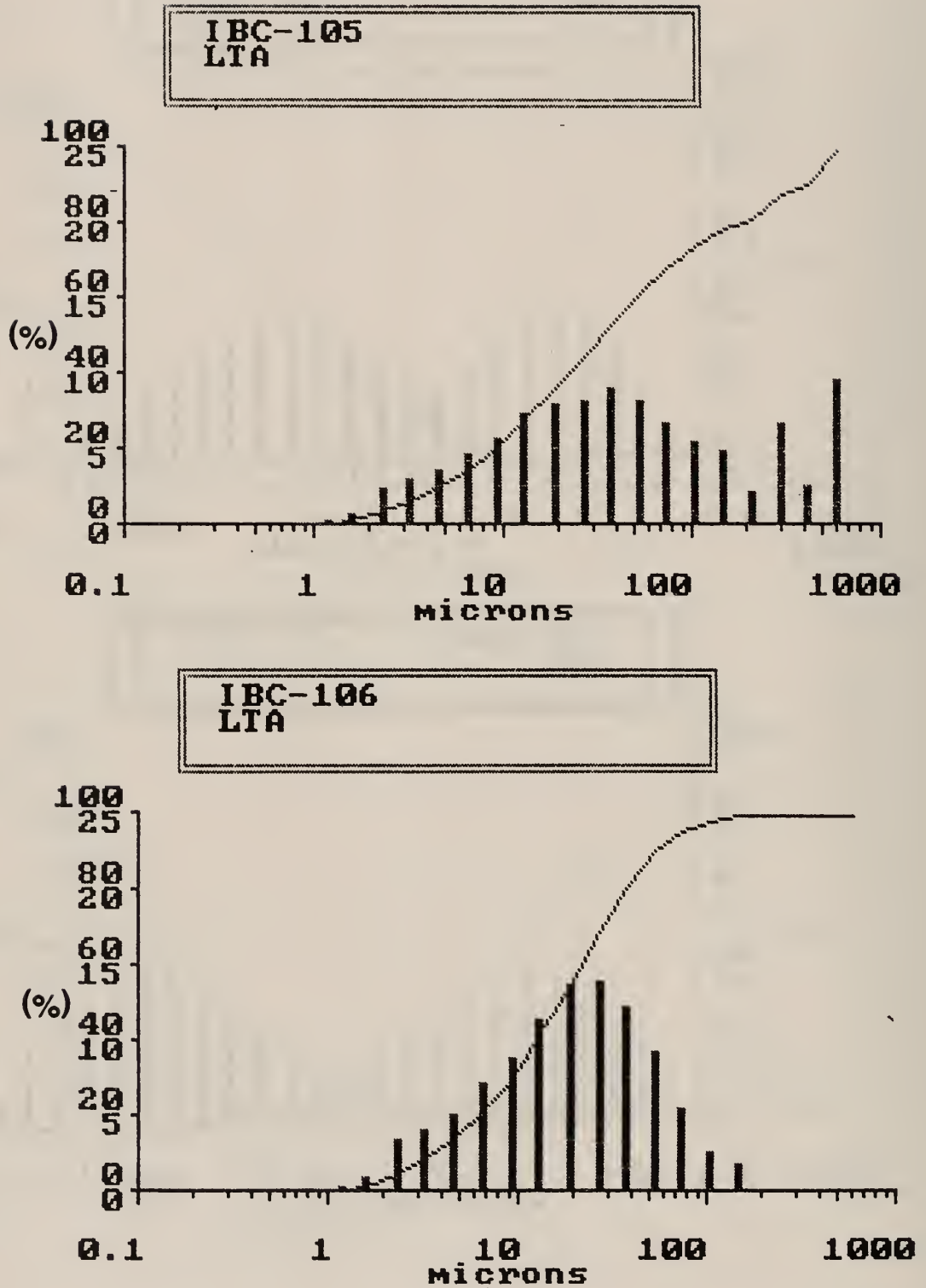


Fig. 10. The frequency histogram of particle size classes and the cumulative size distribution of mineral matter in IBC-105 and IBC-106 coals.

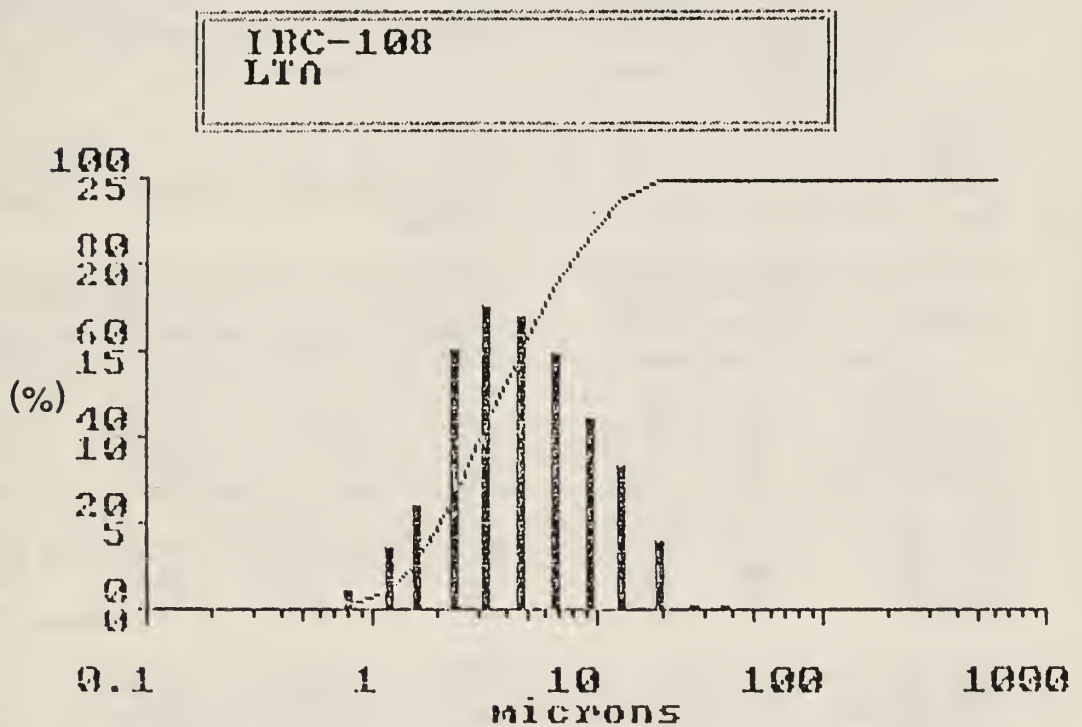
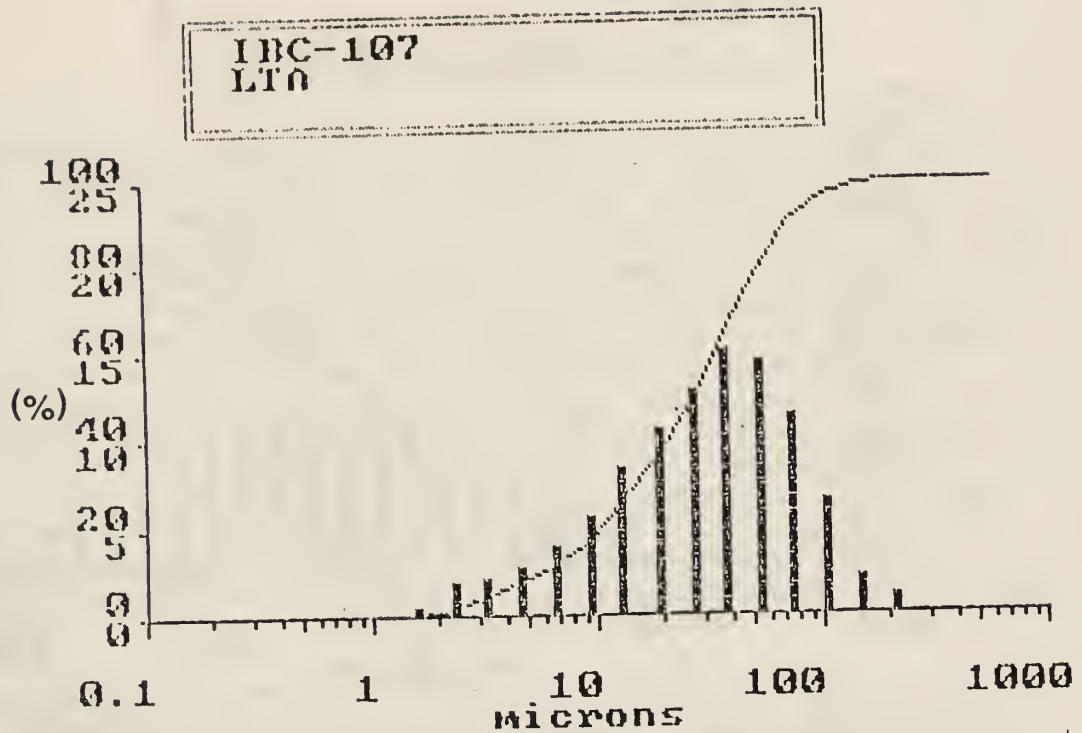


Fig. 11. The frequency histogram of particle size classes and the cumulative size distribution of mineral matter in IBC-107 and IBC-108 coals.

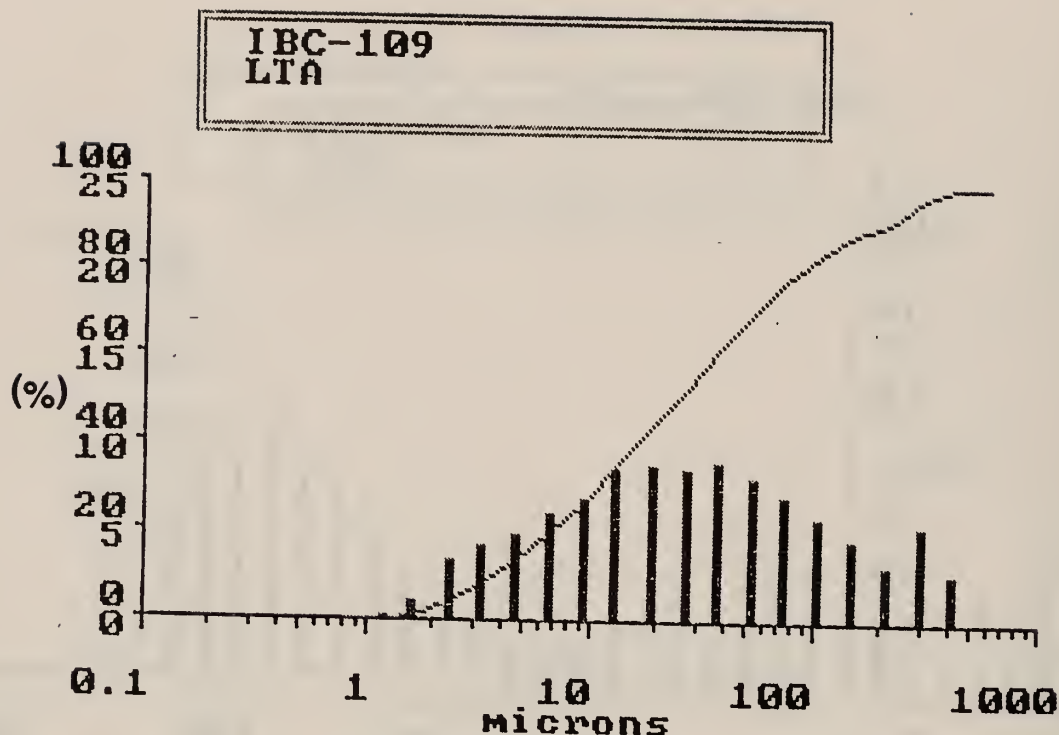


Fig. 12. The frequency histogram of particle size classes and the cumulative size distribution of mineral matter in IBC-109 coal.

Table 5. Particle size distribution of mineral matter in samples from the Illinois Basin Coal Sample Program

| Sample  | Mean size( $\mu\text{m}$ ) <sup>#</sup> |      | Standard deviation ( $\mu\text{m}$ ) | Cum. Distribution (<, $\mu\text{m}$ ) |      |       |
|---------|-----------------------------------------|------|--------------------------------------|---------------------------------------|------|-------|
|         | vol.                                    | area |                                      | 10%                                   | 50%  | 90%   |
| IBC-101 | 43                                      | 11   | 31                                   | 4.1                                   | 22.6 | 96.9  |
| IBC-102 | 81                                      | 11   | 68                                   | 3.9                                   | 21.7 | 292.3 |
| IBC-103 | 86                                      | 9    | 65                                   | 3.2                                   | 19.6 | 311.8 |
| IBC-104 | 116                                     | 22   | 98                                   | 8.4                                   | 58.4 | 317.4 |
| IBC-105 | 126                                     | 15   | 143                                  | 5.5                                   | 39.4 | 480.3 |
| IBC-106 | 29                                      | 11   | 22                                   | 4.3                                   | 19.9 | 62.4  |
| IBC-107 | 42                                      | 16   | 32                                   | 6.8                                   | 31.7 | 88.4  |
| IBC-108 | 8                                       | 4    | 4                                    | 1.8                                   | 4.5  | 12.8  |
| IBC-109 | 69                                      | 12   | 61                                   | 4.2                                   | 27.7 | 214.8 |

<sup>#</sup> The vol. measure is the mean diameter of the measured volume distribution of the tested sample, biased toward the larger particles. The area measure is the mean diameter of the measured area distribution, biased toward the smaller particles.

## CONCLUSIONS AND RECOMMENDATIONS

The organic sulfur distribution as a function of distance from pyrite grains is different for the three untreated coal samples: sulfur increases as one approaches pyrite in two samples (IBC-101 and IBC-102) while it decreases approaching pyrite in the other (IBC-107). The trends are opposite that which is expected if the increased levels were caused by oxidation of nearby pyrite, which would then add elemental sulfur. It may be that the observed trend is not real, that is the spatial resolution of the SEM-EDX data is not sufficient to make any interpretation of the small observed changes. Possibly the trend is real, and the only data that is anomalous is that from the unique IBC-107. Further study of this relation is warranted. Another trend observed for the untreated coals is that at a distance of 12 to 20  $\mu\text{m}$  from pyrite grains, mean organic sulfur content tends to decrease with increasing size of pyrite grains. We interpret these results to indicate that sulfur tends to combine more efficiently with iron to make pyrite than with organic matter during coal formation.

When the coals were pyrolyzed at 550°C, the temperature where pyrite starts decomposing, the organic sulfur content increases near pyrite grains for all three coals tested. These results suggest that sulfur from pyrite grains migrates into adjacent macerals upon charring at 550°C. The same conclusion can be reached by examining the sulfur isotope data. The results of the isotope analyses of organic sulfur in the IBC-107 coal, prior to and after charring, indicate that the organic sulfur remaining in the 550°C chars comprises about 18 percent of the sulfur that was originally pyritic sulfur.

The results of tests of the grain sizes of the mineral matter, reported here for the first time, indicate there is a significant variation in size of minerals from one sample to another, and the method of analysis developed here has much promise for use in coal testing. It has potential use in enabling the prediction of the fineness of crushing that would be needed to liberate a designated portion of the mineral matter. But the observed inconsistencies between the two expressions of the mean size, the volumetric and area bases, must be evaluated further in a future study. In addition, the reproducibility of the method, when applied to minerals in coal, needs to be determined.

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IN MACERALS AND CHARS

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